

An Electrolytic Method for the Preparation of Pure Caus- tic Alkalies for the Laboratory.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

HENRY PHILIP STRAUS.

1905.

EASTON, PA. :
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The author desires to express his gratitude to President Ira Remsen for the profit derived from his instruction.

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INTRODUCTION.

The purpose of this work was to find a practical method by which a laboratory could readily supply itself with pure sodium and potassium hydroxide in any required quantity.

The sodium and potassium hydroxides obtained from the dealers in fine chemicals as a rule contain sufficient impurity to render them unfit for many purposes in both quantitative analysis and the finer preparative work. A laboratory method by which these reagents could be readily prepared in the pure state would remove a source of frequent annoyance and inconvenience.

The method in most general use for preparing pure caustic solutions is to allow the metal to deliquesce over water. The metal is placed in a dish, and becomes coated with a layer of most concentrated hydroxide which interferes with the rapid action of the water on it. A bell-jar or desiccator is used to protect the contents of the dish from the air. In spite of precaution, dangerous explosions are liable to occur when the attempt is made to prepare quickly any considerable quantity of the alkali.

F. W. Küster¹ has devised a method by which large quantities of pure sodium hydroxide from the metal can be prepared more expeditiously than hitherto. Bars of the metal weighing 100 grams or more are placed in a funnel of platinum wire-gauze which is suspended over a flask. The flask is set in the middle of a flat-bottomed dish containing water. The funnel and the flask are enclosed in a bell-jar resting upon the bottom of the dish containing the water. The hydrogen, developed by the action of the water-vapor upon the metal, escapes through the water in the dish, while the solution of the hydroxide, which is also formed at the same time by this action, drips into the flask. The solution thus produced contains 40 per cent sodium hydroxide.

A method of preparing the caustic alkalis from less costly material than the metals is desirable. Hence a number of

¹ Zeit. f. anorg. Chem.

electrolytic arrangements were tested with reference to the economical purification of the commercial materials in quantities sufficient to meet the demands of the laboratory.

Diaphragm Methods.

In the first trials, methods involving the use of diaphragms were employed. The use of diaphragms makes practicable the employment of apparatus of simple construction. Diaphragms of "Pukal paste," and also ordinary porous clay vessels were tried. A solution of commercial sodium hydroxide was the electrolyte used in the experiments which were made. The electrolyte contained large quantities of carbonate, chloride, sulphate, alumina, and silica, besides smaller quantities of other things. In all the experiments made in this direction, the cathode was immersed in pure water, and the anode in the impure solution of the caustic alkali.

The caustic solutions produced by the electrolysis were slightly contaminated by traces of alumina and silica probably derived from the diaphragm. No traces of acids other than silica were found in the products, and, so far as purity was concerned, the alkalis obtained in this way were highly satisfactory. But the objections to the use of diaphragms led to their abandonment. These were the following: (1) The best efficiency is obtained with low current density involving a slow production of the hydroxide. (2) A large part of the electrical energy expended is lost through the re-electrolysis of the pure alkali, and the loss from this source increases with concentration of the solution. It is therefore impracticable to obtain pure solutions of more than very moderate concentration. (3) The resistance of the interposed diaphragm involves the waste of considerable electrical energy.

Mercury Cathode Processes.

The method next tried for the preparation of pure caustic alkalis was a mercury cathode process. Davy,¹ in the year 1810, discovered that when mercury is made the cathode in the electrolyses of solutions of the hydroxides and salts of the

¹ Phil. Trans. 1808-1810.

metals of the alkalis, amalgams are formed, which on treatment with water decompose with the production of caustic alkalis, hydrogen and mercury. A successful method for preparing caustic alkali on the commercial scale by means of a mercury cathode was not devised until over eighty years after this discovery.

Atkins and Applegarth (D. R. P., No. 64409), in the year 1891, and Sinding-Larsen (U. S. P., No. 525555), the following year, introduced processes using a mercury cathode, which, with the improvements of the next few years by Castner (U. S. P., No. 528322), Kellner (U. S. P., Nos. 590548, 588276 and 634408), Rhodin,¹ Solvay (D. R. P., No. 104,900) and others developed this method to such an extent, that it seems likely to supplant all others for the manufacture of caustic alkalis.

The successful employment of mercury as a cathode depends mainly upon the proper solution of three problems: (1) The quick withdrawal of the amalgam when formed, from contact with the solution undergoing electrolysis; (2) the transference of the amalgam to the compartment of the apparatus, where it is decomposed by water into the hydroxide, mercury and hydrogen; and (3) the quick return of the mercury resulting from the decomposition of the amalgam to its original position. For a continuous process, it is essential that the three processes mentioned above should maintain an equal pace.

The amalgam must not be allowed to accumulate in the mercury employed as cathode, since mercury containing less than 1 per cent of alkali metal is of a pasty consistency, while with 2 per cent it is solid. Moreover, provision must be made for a sufficiently rapid decomposition of the amalgam. If the amalgam is allowed to accumulate, it floats upon the mercury, and is not easily transferred to the compartment of the apparatus in which the decomposition takes place.

A number of devices are employed for removing the amalgam from the place of its formation to that of its decomposition. These are: (1) centrifugal motion, as in the Rhodin process;²

¹ L'Industrie, Jahrg. 1900, s. 79.

² Ahrens-Electro-Chemie, s. 427, 2nd Aufl.

(2) a rocking or tilting motion which transfers the mercury alternately from one compartment of the apparatus to the other, as in the Castner process (U. S. P., No. 518135); and (3) a continuous stream of mercury flowing from the electrolyzing and oxidizing compartments of the apparatus and back again, as in the Solvay process (D. R. P., No. 104900).

The chief methods employed for the decomposition of the amalgam into caustic alkali and mercury are: (1) by stirring with water, as in the Sinding-Larsen process (U. S. P., No. 525555); (2) by treatment with steam; and (3) electrically, as in the Castner (U. S. P., No. 518133), Kellner (U. S. P., No. 631463), Solvay (D. R. P., No. 104900), and Rhodin¹ processes.

Description of the Apparatus.

An apparatus was constructed in which tests could be made of many of the principles involved in the most successful mercury cathode processes. Fig. 1 is a longitudinal cross-section of the final form of the apparatus which was found to best suit the purpose of the investigation.

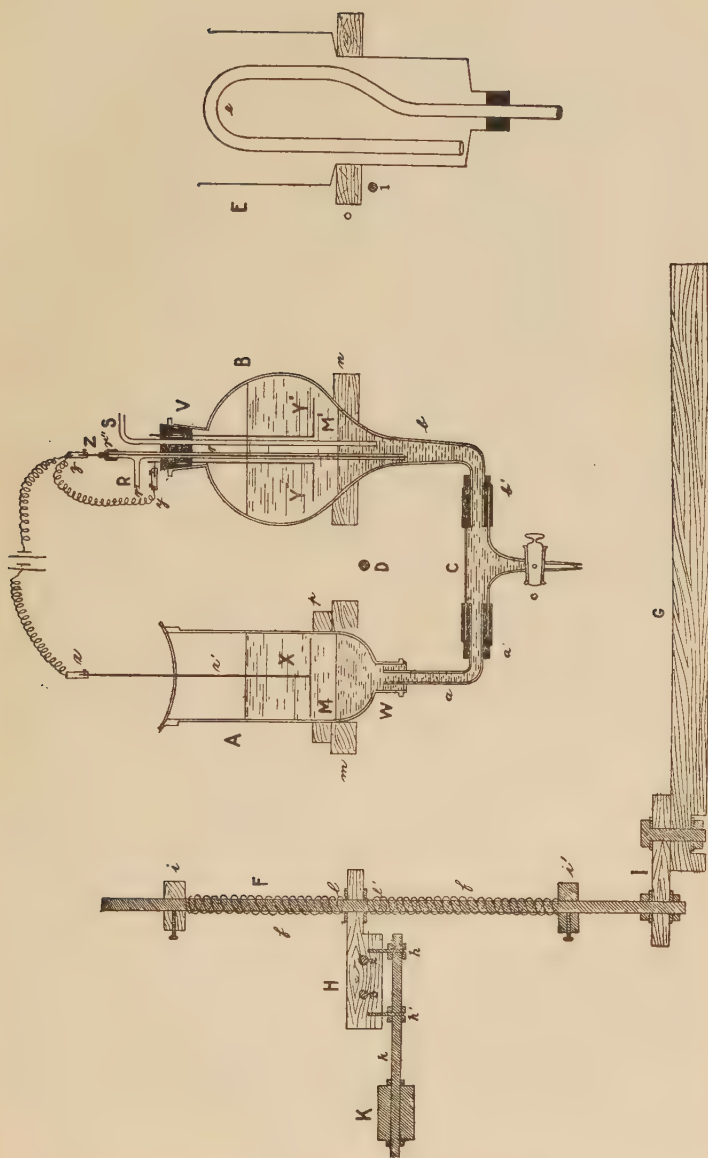
A is an inverted bell-jar with a capacity of about one liter, and is the electrolyzing cell.

B is a funnel-shaped bulb having a capacity of about one and a half liters, and is the oxidizing cell. The bulb is made of a glass very resistant to alkali.

C is a glass 150 mm. in length, and about 20 mm. in diameter, and serves to connect A and B.

The connection of A and B is made as follows: *a* is a glass tube from A, which is bent at right angle about 75 mm. from end. The other end passes through the rubber stopper, W. The stopper, W, is firmly secured in its position by wiring, and winding with adhesive insulating tape. *b* is the stem of B, which is also bent at right angle, about 75 mm. from its end, to correspond to the tube, *a*. *a* and *b* are secured in their places in C by pieces of heavy rubber tubing, which are tied with waxed shoemaker's thread, and supported by winding with insulating tape. The joints thus made are perfectly

¹ Chem. Ztschr. I, s. 596 (1902).



tight, and elastic enough to prevent any danger of breakage by an accidental jarring. A stop-cock, *c*, fitted into the side of the tube, *C*, permits the easy removal of the mercury from the apparatus.

A and B are held firmly upon a skeleton framework by means of blocks and clamps.

The frame (see Fig. 2) consists of two hard-wood strips, $36'' \times 2\frac{1}{2}'' \times \frac{5}{8}''$, clamped at a distance of 5'' apart by the two $\frac{3}{8}''$ bolts, 1 and 2. Two small wooden strips serve as supports for the blocks, *m*, *n*, and *o*.

The blocks, *m* and *n*, are bored and formed to exactly fit A and B respectively. A is secured in its place in the block by the adjustable wooden collar, *p*, which rests upon *m*.

The framework rocks up and down about an axle, *D*, which passes through brass bearings fastened upon the inner sides of the frame. The axle, *D*, which is a $\frac{3}{8}''$ bolt, is fixed to two wooden standards attached to the opposite sides of the base, *G*.

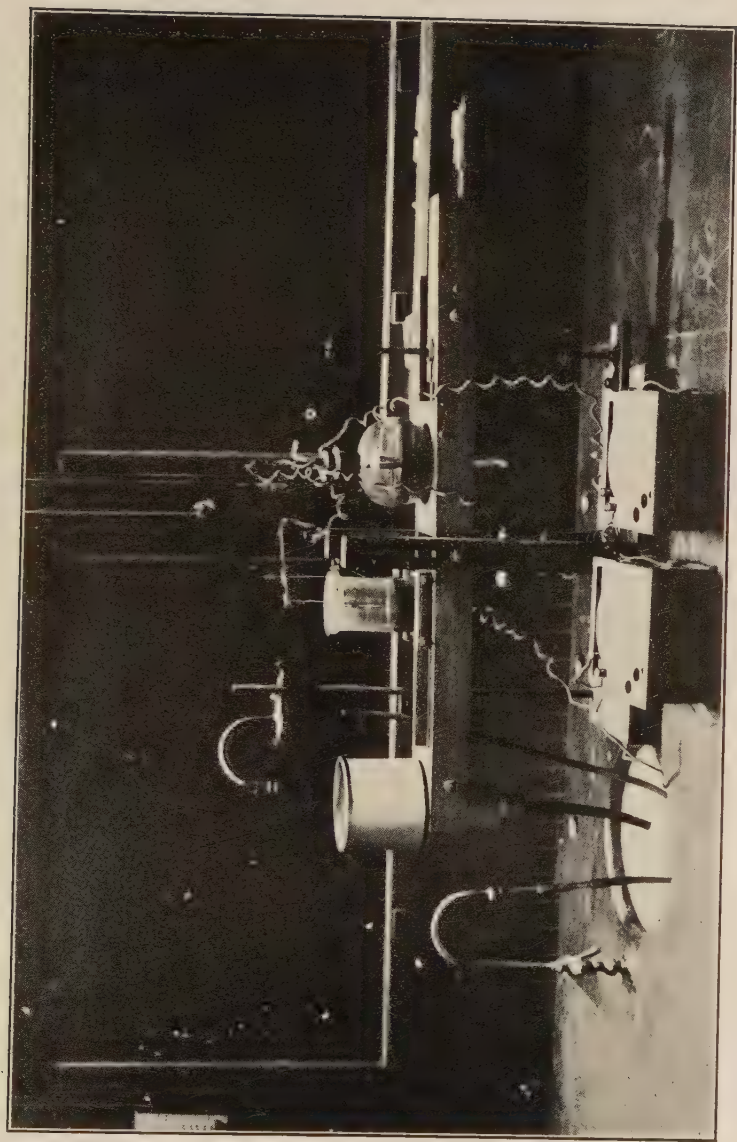
The motive-power for rocking the framework is a siphon-cup, *E*, which has flowing into it, constantly, a small stream of water through a bent tube attached to the hydrant. The tube is held in position by a clamp attached to an iron rod in the base, *G*.

E is made of galvanized sheet-iron, and has a capacity of about four liters. The rate of filling the cup, *E*, is controlled by regulating the flow of water from the hydrant, while the rate of emptying it is determined by the diameter of the siphon-tube, *e*. The cup is held in place on the frame by the wooden block, *o*, which rests upon the strips previously mentioned, and is fastened in its place by screws.

The amplitude of the swing of the working part of the apparatus is regulated by the two spiral springs of steel wire, *f* and *f'*, upon a steel standard, *F*, which passes through the frame from the base, *G*, to which it is bolted.

The standard, *F*, is a $\frac{3}{8}''$ steel rod 24'' in length. The springs upon *F* press against two large iron washers which cover a slot in the block, *H*, through which the standard, *F*, passes.

The block, *H*, is attached firmly to the moving frame by the



two $\frac{3}{8}$ " iron bolts, 2 and 3, which run through it and the sides of the frame.

Any movement of the frame causes an alternate compression and expansion of the springs along the rod. This gives steadiness to the movements of the frame.

By means of a sliding weight, K, upon a threaded $\frac{3}{8}$ " iron rod, *k*, which is attached to the block, H, by means of two screw-eyes, *h* and *h'*, a proper adjustment of the balance of the moving frame is obtained.

The base, C, consists of a piece of heavy wood, $24'' \times 8\frac{1}{4}'' \times 1\frac{3}{4}''$, and is raised slightly from the table top by means of two narrow strips of wood nailed to the bottom to allow the circulation of air underneath, and thus prevent warping. I is a small wooden extension bolted to the base, and carries the standard, F. Two wooden standards from the sides of the base serve as supports for the axle, D. These are slotted vertically to permit the adjustment of the apparatus in higher or lower positions.

The anode, *x*, is a perforated platinum disc, 7.5 cm. in diameter, which is attached to a platinum rod, *x'*. The electrode is kept in place by a clamp attached to a vertical rod in the block, *m*. By this arrangement, the anode and the bell-jar move together with the frame, as a movement of the anode in the bell-jar, A, is objectionable.

The bell-jar, A, is covered by a large watch-crystal with a small hole in the centre, through which passes the rod, *x*. The crystal prevents the spraying into the room of the electrolyte by the oxygen gas developed at the anode during electrolysis.

The nickel rod, Z, dips into the mercury, MM' as a whole thus becomes the cathode to the anode, X. The rod is insulated where it passes through the liquid in *b* by a small rubber tube, which slips over it, and extends into the mercury.

The cathode of the oxidizing cell, B, consists of four nickel plates, Y, Y', etc., each plate being 2.5 cm. $\times$ 5 cm. The plates are attached to strips of nickel which pass through slits in the rubber stopper, V, and project 20 mm. above the stopper, where they are joined together by a copper wire. The nickel plates thus become the cathode to which the mercury, MM',

is the anode. Each plate and its strip are cut in one piece from sheet-nickel. The surfaces of the plates are curved to allow the hydrogen gas formed there to readily escape.

At r'' , an air-tight joint is made where the nickel rod leaves the T-tube, R, by slipping a piece of heavy rubber tubing over the rod and the end of the T-tube, and tying. The hydrogen gas developed at the nickel cathode escapes from B by r , out through the arm of the T-tube at r' . Attached to the arm of the T-tube at r' is a small U-tube of soda-lime to remove carbon dioxide from the air which also enters the apparatus at this point.

S is a siphon-tube for removing the pure caustic solution from B without contact with the air.

x , y , and z are binding-screws. x and z are connected respectively with the positive and negative poles of either a dynamo or storage battery. By connecting y and z , a battery is formed in which the mercury, M' , is the anode, and the nickel plates, Y , Y' , etc., are the cathode.

From 350 to 400 cc. of mercury are required for the proper working of the apparatus. In the bell-jar, A, enough of the solution of the electrolyte is employed to keep the anode, X, always well covered, 300 to 400 cc. of solution being ample for this purpose.

Saturated solutions of rather impure commercial hydroxides were used as the electrolytes. These solutions are kept saturated by occasionally adding solid hydroxide to the solution.

Method—The Decomposition of Sodium Amalgam by Heating in Contact with Water.

Preliminary experiments were tried, in order to ascertain the best procedure for the decomposition of the sodium amalgam in the oxidizing cell of the apparatus. The first method was to note the effect of heat upon the rate of decomposition of the sodium amalgam in B, as compared with its rate of formation in A.

In the first method tested, the arrangement for the decomposition of the amalgam in B, which is formed in A, was not

that already described as employed in the final form of the apparatus; instead, a heavy platinum-wire dipped into the mercury in B. The anode was the platinum disc, X, already mentioned. The electrolyte used was a saturated solution of commercial sodium hydroxide. It is essential to keep the solution of the electrolyte fully saturated with caustic alkali, in order to prevent the decomposition of the sodium amalgam at the surface of contact between the mercury and the solution. With saturated solutions of sodium hydroxide, practically no decomposition of the sodium amalgam was observed at the surface of contact in A.

The amalgam, which is formed in A, is carried through the mercury to the bulb, B, by the rocking motion of the apparatus. The amalgam which diffuses into B, being lighter than the mercury, rises to the surface in B, and forms floating islands on the surface of the metal. These masses of amalgam are rather slowly decomposed in contact with the water at ordinary temperature. Considerable decomposition, due to local action, takes place at the contact of the mercury and the wire.

The amalgam also accumulates in B about the platinum wire both at and below the surface of the mercury. The movements of the mercury cause a part of the wire to be alternately exposed to the water and the mercury, and it was observed that the rise and fall of the mercury along the wire apparently detached from its sides the amalgam, which appeared to be the principal source of the floating masses of amalgam previously referred to. Starting with mercury free from amalgam, this accumulation is noticed almost immediately upon closing the circuit. This tendency on the part of the amalgam to accumulate about the platinum wire is no doubt an important factor in the transportation of the sodium from A to B.

As the rate of decomposition of the amalgam by contact with water at ordinary temperatures is very slow, an attempt was made to hasten the reaction by warming the liquid contents of the bulb, B, with an electric graphite stove, such as is described by Morse and Frazer.¹ The stove surrounded the

¹ *Am. Chem. Jour.*, **32**, 93.

bulb, and by means of it, any required temperature could be readily maintained.

With temperatures ranging between 50 and 66° C., and the current employed averaging 2.7 amperes, the amalgam was decomposed from 22 to 36 per cent as fast as it was formed. The surface of the mercury in contact with the water in B had an average area of about 90 sq. cm. Under these conditions there is a constant accumulation of amalgam in the mercury. In other words, the decomposition of the amalgam does not appear to keep pace with its formation.

The heating of the water in order to hasten the decomposition of the amalgam is objectionable, owing to increased action of the alkali on glass at higher temperatures. Further objection to the arrangement used in this case is the waste of electrical energy in maintaining higher temperatures, the amount used for this purpose being about three times as great as is required for the electrolysis of the hydroxide.

Method—The Decomposition of Amalgam by Short-Circuit After Charging.

In the second series of experiments, the platinum-wire, which dipped into the mercury in B, was replaced by an iron rod bearing an iron disc about 20 mm. from its lower end. As in the previous experiments, the rod and disc dipped into the mercury during the formation of the amalgam. After considerable quantities of amalgam had accumulated in the mercury, the main circuit was opened, the iron rod was pulled out of the mercury in B into the water above, the platinum anode was pushed down into the mercury in A, and the two electrodes were then connected.

A battery is thus formed in which the amalgam plays the part of a dissolving anode, and the iron disc, the cathode. The rate of decomposition of the amalgam is found by placing an ammeter in the circuit. Owing to the amalgamation of the iron cathode, while charging the mercury with sodium amalgam, the current, with the arrangement just described, never amounted to more than 0.35 ampere. The low rate of decomposition is due to the polarization caused by the

amalgamation of the iron cathode, the effect being the same as in a cell having both electrodes of the same material.

Though it required a very long time to completely discharge the mercury of the amalgam with the iron cathode thus amalgamated, nevertheless, without taking into consideration the time necessary to completely decompose the amalgam, an idea was obtained as to the probable current efficiency of the method.

Table I gives the results obtained by this method, in three determinations made in the sodium hydroxide apparatus, and one determination made in another apparatus of the same kind, in which pure potassium hydroxide was formed.

Table I.

No. of experiments.	Actual yield. Grams.	Theoretical yield. Grams.	Current efficiency. Per cent.	Substance. Sodium hydroxide.
1	151.1127	156.6234	96.85	Sodium hydroxide
2	36.3272	37.3250	97.85	Sodium hydroxide
3	117.6667	122.0215	96.43	Sodium hydroxide
4	28.7306	30.5641	94.00	Potassium hydroxide

Notwithstanding the high current efficiency obtained, the objections to this method, as tested, are sufficient to justify its abandonment. A long time is necessary to prepare the solutions of the hydroxides, owing to the amalgamation of the iron cathode. The pure caustic solutions are contaminated by the iron hydroxide, which is formed by the combined action of the caustic solution and the oxygen of the air upon the iron cathode. The platinum anode, X, is amalgamated on its withdrawal from the mercury, M', where it is placed during the discharge of the amalgam. On further electrolysis of the caustic solution in A, oxides of mercury are found at the amalgamated anode, X, which discolor the solution of the electrolyte. Another objection to the employment of this method is that the process is not continuous.

In the method tried next, the above-mentioned difficulties were avoided by the use of the very simple arrangement in the bulb, B, which was employed in the final form of the apparatus. In this arrangement, which has already been described, it was

found necessary to insulate the nickel rod, Z, which dips into the mercury in the bulb, B, in order to prevent the amalgamation of the nickel cathode. The amalgamation of the cathode is caused by the mercury creeping up the rod through the caustic solution to wherever the nickel strips or plates of the cathode happen to touch it. This creeping of the mercury along the nickel rod through the solution of the caustic alkali was similarly observed when the iron rod was used.

Method—The Decomposition of Amalgam by a Minor Circuit during Charge.

In this method, the final form of the apparatus previously described was employed (see Fig. 1). By a very simple system of electrical connections, it was possible to combine the two operations of formation and decomposition of the amalgam in such a manner, as to form a continuous process within the apparatus, and at the same time, to permit the use of higher current densities.

The connections were made in the following manner: The platinum anode, X, in the bell-jar, A, and the nickel rod, z, in the bulb, B, are respectively connected by the binding screws, x and z, to the positive and negative poles of a dynamo or storage battery. The nickel rod, z, and the nickel plates, Y, Y', etc., which form the cathode in the bulb, B, are connected by the binding screws, y and z, with a short piece of heavy flexible wire.

There are thus established two independent circuits which will be designated hereafter as the major and minor circuit.

The current in the major circuit flows from the positive pole of the dynamo or storage battery to the platinum anode, x, through the solution of the impure caustic solution to the mercury, MM', and back again, by the nickel rod, z, to its source. This current electrolyzes the impure caustic solution in A, with the consequent formation and storage of amalgam in the mercury.

The current in the minor circuit flows from the mercury, M', in the bulb, B, through the solution of the pure caustic to the nickel plates and back to the mercury, M', by means

of the nickel rod, *z*. The current in this circuit is produced by the decomposition of the amalgam which is diffused by the rocking motion from A into B.

As the nickel rod, *z*, which the two circuits have in common, offers practically no resistance to either circuit, the two circuits are entirely independent of each other.

The two cells, A and B, are only dependent upon each other in so far as B depends upon the amalgam formed in A for its energy, and A depends upon B to prevent the accumulation of amalgam in the mercury.

The effect of the apparatus as a whole is similar to a storage battery, which is charging and discharging at the same time. In this method, the charge and discharge of the mercury balance each other, if the current density used in A does not exceed the discharging capacity of B.

The discussion of the discharging capacity of B will be taken up later. Tables No. 2 and No. 3 give the results of careful tests as to the efficiency of the apparatus for the preparation of pure sodium and potassium hydroxides by this method.

In these experiments, a copper voltameter was used to determine the current efficiency.

Table No. 2.

No. of experiment.	Copper deposited in voltameter. Grams.	Actual yield of NaOH. Grams.	Theoretical yield of NaOH. Grams.	Current efficiency. Per cent.
1	20.4523	26.6587	26.7577	99.53
2	23.4357	28.6948	29.5151	97.22
3	13.6476	17.1849	17.2879	99.40
4	286.1425	346.0056	350.3657	98.80
Mean,				98.74

Average current, 5 amperes.

Average electromotive force, 4.3 volts.

Average resistance, 0.86 ohm.

Average area of mercury cathode, 42.2 sq. cm.

Area nickel cathode, 50 sq. cm.

Current density at mercury cathode, 11.8 amperes.

Theoretical electromotive force, 2.54 volts.

Efficiency electromotive force, 60 per cent.

Electrical energy, per hour, 21.5 watts.

One kilowatt, 342.8 grams sodium hydroxide.

One kilogram sodium hydroxide, 2.9 kilowatts.

Table No. 3.

No. of experiment.	Copper deposited in voltameter. Grams.	Actual yield of KOH. Grams.	Theoretical yield of KOH. Grams.	Current efficiency. Per cent.
1	20.4525	34.2564	36.1099	94.37
2	23.4357	38.7521	41.3775	93.65
3	13.6476	23.5656	24.0958	97.80
4	312.5891	536.2704	551.8851	97.22

Mean, 95.76

Average current, 5 amperes.

Average electromotive force, 4.05 volts.

Average resistance, 0.81 ohm.

Average area of mercury cathode, 42.2 sq. cm.

Area of nickel cathode, 50 sq. cm.

Current density at mercury cathode, 11.8 D_{100} amperes.

Theoretical electromotive force, 2.42.

Efficiency electromotive force, 60 per cent.

Electrical energy, per hour, 20.25 watts.

One kilowatt, 496.5 grams potassium hydroxide.

One kilogram potassium hydroxide, 2 kilowatts.

The result of the tests made by this method show that the apparatus can be satisfactorily employed for the preparation of pure sodium and potassium hydroxides in quantities sufficient to meet the ordinary demands of the laboratory for pure caustic alkalis.

The average current efficiency obtained was 98.74 per cent for sodium, and 95.76 per cent for potassium hydroxide.

The electromotive force required for the electrolysis with a mean current of 5 amperes averaged 4.3 volts for sodium, and 4.5 volts for potassium hydroxide. The theoretical values for the electromotive required to electrolyze aqueous solutions of sodium and potassium hydroxides, are, respectively, 2.54 volts for sodium, and 2.42 volts for potassium hydroxide. This gives an energy efficiency of about 0.60 per cent.

A large part of the energy which is expended is lost in overcoming the resistance of the solutions to the passage of the current. Owing to the movement of the mercury in the two cells with the swing of the apparatus, the resistance in this apparatus varies with the change in distance between the platinum anode and the mercury cathode in the cell, A. In consequence of this constant variation of the resistance in A, only an approximate value of the current is obtained by averaging the readings of an ammeter placed in the circuit. In order to determine the current efficiency more accurately, a copper voltameter was used to measure the current.

With the distance between the platinum anode and mercury cathode varying from 1 to 4 cm., and the current averaging 5 amperes, the mean resistance for the sodium hydroxide apparatus was 0.86 ohm, and for the potassium 0.81 ohm.

In practice, a current from a storage battery was passed, in series, through both the sodium and potassium hydroxide apparatus, and the voltameter, thus making one deposition of copper serve to measure the quantity of current which had been used by each apparatus. The values taken in the estimation of the current efficiency were:

One ampere hour: 1.18548 grams copper.
 1.493 grams sodium hydroxide.
 2.085 grams potassium hydroxide.

A determination of the current efficiency was made in the following manner:

A measured quantity of water was placed in the bulb, B. In general, a current of 5 amperes was run from five to eight hours on a stretch, with both the major and the minor circuits closed. On breaking the current in the major circuit, it was necessary to allow the small accumulation of the amalgam in the mercury to become completely discharged, before a determination of the yield of the hydroxide could be estimated. When completely discharged, the bulb contents were thoroughly mixed by plunging the nickel cathode up and down. The solution of the pure caustic was withdrawn by a graduated pipette, and titrated with standard sulphuric acid. By introducing a volume of water into the bulb, equivalent to that

of the hydroxide withdrawn for analysis, the volume of the solution in the bulb was kept practically constant, and it was possible to estimate, at any time, the amount of pure alkali in solution.

The time required, after breaking the major circuit, for the complete discharge of any amalgam, which may have accumulated in the mercury during the charge, was in general less than an hour, and sometimes not over half an hour. A test was made to see if the discharge of this accumulation of amalgam was complete. Within half an hour after the evolution of hydrogen at the nickel cathode had ceased, and no current could be observed passing through a milliammeter in the circuit, about 200 grams of mercury were withdrawn from each apparatus, and violently shaken with hot water for half an hour. On the addition of phenolphthalein, no trace of color was observed, showing the completeness of the discharge.

By means of an ammeter placed in the minor circuit, the rate of decomposition of the amalgam could be approximately measured. It was found that the current in the minor circuit averaged but little less than the major current. Though the current of the minor circuit is less than the current of the major circuit, there is no accumulation of amalgam in the mercury for the current employed. This is in consequence of the decomposition of the amalgam in other ways, than by the current of the minor circuit. The available supply of amalgam in the mercury is insufficient to give rise to a rate of decomposition, by the current of the minor circuit, which would be the equivalent of the rate of formation of the amalgam by the current of the major circuit.

The principal way in which the amalgam is decomposed other than by the current of the minor circuit, is by contact with water of masses of amalgam floating on the mercury in B. This decomposition does not cause a loss in the current efficiency.

There are, however, two sources of loss in the bell-jar, A, which affect, also, the current efficiency. The first is the oxidation of the amalgam at the surface of the mercury by

the oxygen which is formed at the platinum anode, and the second is by contact of the solution of the electrolyte at the surface of the mercury.

The loss of current efficiency, by the contact of the electrolyte at the surface of the mercury, is very small at ordinary temperatures, if the solution is kept saturated with the caustic alkali.

The resistance of the caustic solutions in A, during the electrolysis, is sufficient to give a marked heating effect. With a current of 5 amperes, the liquid contents of A maintained a temperature from 15° to 20° C. higher than the temperature of the room.

The effect of the rise in temperature upon the rate of decomposition of the amalgam, at the surface of contact between the mercury and the electrolyte, slightly increased the decomposition in the case of sodium hydroxide, and very noticeably increased the decomposition for potassium hydroxide. This would partly account for the difference in the current efficiencies which were obtained, the average efficiency for sodium hydroxide being about 3 per cent higher than for potassium hydroxide.

Starting with distilled water in the bulb B, the resistance of the cell is so great, that practically no decomposition can take place at the outset. Through the accumulation of floating masses of amalgam upon the surface of the mercury in B, there is soon enough decomposition by their contact with the water, to start the decomposition by the current of the minor circuit, which quickly attains a magnitude that prevents the accumulation of any considerable excess of amalgam in the mercury.

With a moderately concentrated solution in B, and with the mercury completely discharged, on closing the major circuit, the current in the minor circuit rises gradually, until the accumulation of the amalgam in the mercury reaches a point where the decomposition of the amalgam in B keeps pace with its formation in A. With a current of about 5 amperes, this point is reached in about one hour. A rough estimate was made of the amount of sodium which could be

present in the mercury when the current in the minor circuit had reached this maximum point. The determination was made when this maximum point had been reached within an hour with a current in the major circuit of about 4.5 amperes. The current in the minor circuit was averaged by means of an ammeter placed in the circuit. The amount of sodium present in the mercury was somewhere in the vicinity of 1 part of sodium to 6000 parts of mercury, or about 0.017 per cent. Castner¹ estimated that the amount of sodium present in the mercury, as employed in his process, was less than 0.02 per cent. Castner employed a current density a little higher than was used in this experiment.

A test was made to find what effect the current in the major circuit had upon the current of the minor circuit when the current in the former circuit was broken. An ammeter was placed in the minor circuit, the current of which was allowed to reach its maximum point. This condition would make the current in the minor circuit most sensitive to any effect produced by breaking the major circuit. The current in the minor circuit was slightly lowered by breaking the major circuit. This showed that a slight shunt from the current of the major circuit had been sent through the cell, B. This shunt current is due to the very small resistance which the nickel rod introduces into the major circuit. Though the resistance of the nickel rod is very small, yet the resistance of the cell, B, is still small enough to cause the current of the major circuit to divide, sending a very small shunt through the minor circuit, from the mercury, M', to the point, z, where the two circuits meet. This shunt of the major current was made the basis of another method which will be described later.

By this method, solutions of pure sodium and potassium hydroxides of any concentration may be readily prepared. When the solutions of the pure hydroxides in B have been concentrated almost to saturation by the continual discharge of the amalgam by the current of the minor circuit, a point is reached where the discharging current grows smaller. Under

¹ H. Y. Castner : Eng. Min. J., Sept. 22, 1894.

similar conditions, both the discharging currents and the solutions of the concentrated sodium and potassium hydroxides acted differently. In the case of sodium hydroxide, with a charging current of 5 amperes, the discharging current fell gradually from a maximum of 4.5 amperes to about 0.1 ampere. The solution thus obtained was very viscid, and on removal from the bulb, and cooling with ice-water, sodium hydroxide crystallized out in such large quantities, that the liquid became nearly solid.

With the potassium hydroxide solution, with a charging current of 5 amperes, and a discharging current of nearly 4.5 amperes, the discharging current, near the saturation point, fell gradually until it reached about 2.25 amperes, at which point, it again became steady, while pure potassium hydroxide began to come out of solution in fine crystals, and continued to do so, without affecting the rate of discharge of the amalgam by the current of the minor circuit. This evidently is a method for readily preparing pure crystallized potassium hydroxide in quantity without the further concentration of its solution outside the apparatus.

The time required for the preparation of such solutions by this method is not very great if proper precautions are taken. It is absolutely essential that the amalgamation of the nickel cathode should be avoided. Unless the nickel rod is insulated, the mercury will creep along its sides, and amalgamate the cathode whenever the two happen to touch. The resistance in both circuits should be avoided as much as possible, so as to obtain the highest current efficiency and the maximum discharging capacity. The area of the nickel cathode should be made as large as possible, and brought as close to the surface of the mercury anode as is permissible. Owing to the irregularities which the rocking movement introduced into the flow of the current, the swing of the apparatus should not be greater than is necessary to secure the proper transportation of the amalgam from A into B. A swing, which caused a rise and fall of the mercury from 2.5 to 3 cm., was found to be sufficient for that purpose. A rate of one complete swing per minute and a half was found to be rapid enough to give the

requisite movement. The solution of the electrolyte in A should be kept saturated by placing sticks of solid hydroxide into the bell-jar from time to time. The use of a saturated solution of the electrolyte decreases the amount of decomposition of the amalgam by their contact. The apparatus will afterwards require but little attention, and the highest efficiency will be obtained, by observing these simple precautions at the beginning. By placing sufficient solid hydroxide in the bell-jar, the apparatus will take care of itself over night.

In an apparatus having a capacity of that used in this work, by observing the above precautions, a current of 5 to 6 amperes can be employed without an excessive accumulation of amalgam in the mercury, the quantity of the pure hydroxides produced will be about 8 grams of sodium and 11 grams of potassium hydroxide per hour, and, when running continuously, about 204 grams of sodium and 284 grams of potassium hydroxides every twenty-four hours.

By a modification to be taken up later, it was found practicable to greatly increase the capacity of the apparatus with but a slight increase in the expenditure of energy.

Owing to the high current efficiency obtained, and the low electromotive force required, the pure hydroxides can be prepared from the impure materials at a very low cost. From Tables Nos. 2 and 3, it is seen that one kilogram of pure sodium hydroxide requires for its preparation 2.9 kilowatts, and one kilogram of potassium hydroxide requires about two kilowatts. The cost of electricity in this laboratory is 2.5 cents per kilowatt, which makes the expense of the purification per kilogram, 7.25 cents for sodium, and 5 cents for potassium hydroxide.

The principles involved, which make the preparation of pure sodium and potassium hydroxides by this process a success are, of course, not new, yet their application to the problem in hand is believed to differ from other processes, using the same principles.

Primary and secondary amalgam batteries have long been known and used both for the generation of electrical energy

and for the preparation of the caustic alkalis (A. S. Hickley, U. S. P., No. 356640, 1887). The application of the principles of the amalgam battery has been the subject of many patented processes, as those of Kellner, Rhodin, Solvay and others. The chief differences in these processes lie rather in the mechanical construction of the apparatus employed, than in an entirely new application of the principles of the amalgam battery.

The use of the rocking motion for the transportation of the amalgam formed in A, into B, is somewhat similar to that employed in the apparatus devised by Castner (U. S. P., No. 518135). In the Castner process, a moving body of mercury is made to completely separate the products of electrolysis. The cell is divided into three compartments by partitions which fit loosely into grooves in the bottom, and is given a slight rocking motion, which causes the mercury to flow continuously from side to side through the middle compartment alternately from the outer two. The outside compartments contain the electrolyte and anodes of carbon, and the middle compartment contains an iron cathode and the caustic solution. The electric current traverses the electrolyte, forming amalgam. By the rocking, the amalgam continuously passes back and forth through the middle compartment, where the mercury acts as anode during the passage of the current to the cathode, the alkali metal being liberated, and going into solution as the hydroxide.

In the Castner process, as the electrical efficiency is always 100 per cent, any loss in the current efficiency would cause an oxidation of the mercury anode by the electrolysis of the pure caustic solution, and, unless there is present in the mercury a sufficient amount of the alkali metal, oxides of mercury would be produced which would contaminate the solution of the caustic alkali. Owing to the loss of amalgam from the mercury by loss of current efficiency in the electrolyzing cells, it is necessary to keep the mercury enriched with sufficient alkali metal as to prevent the formation of the oxides of mercury.

In the apparatus as constructed it was possible to try a modified Castner process.

In the Castner apparatus the mercury flows comparatively unrestricted from compartment to compartment, with very little fall. In this apparatus, the mercury passes between the two compartments through the narrow tube, C, with a greater fall, which causes a considerable pressure during the passage, and effects a more thorough mixing of the mercury with the amalgam than is to be had in the regular Castner apparatus.

By connecting the platinum anode, X, with the positive pole of a storage battery, and the nickel cathode, YY', etc., with the negative pole of the battery, an arrangement is had which is similar to the Castner process. A comparative test was made of the Castner process and the method last described as employed in the apparatus.

A constant electromotive force was obtained from a storage battery, by charging the battery at the same rate as the discharge. When uniform conditions of current and temperature were obtained in the apparatus, the current was measured quantitatively by a copper voltameter. The test of each method lasted four hours and the conditions remained practically constant during the entire period.

The results are found in Table No. 4, below.

Table No. 4.

No. of experiment.	Time Hours.	Copper deposited in voltameter in 4 hours. Grams.	Current Amperes.	Difference in potential. Volts.
1	4	22.7775	4.834	4.1
2	4	20.7330	4.372	4.3
Difference		2.0440	0.462	0.2

Experiment No. 1 shows the results obtained by our method.

Experiment No. 2 shows the result of the Castner process under similar conditions. The experiments show that the current efficiency, as measured by the copper voltameter, is about 10 per cent greater for our process than for the Castner method, and also, that the electromotive force is about 5 per cent less.

Method—The Decomposition of Amalgam by a Shunt Circuit during Charge.

Though the quantity of pure hydroxide produced in a single apparatus by the previous method is sufficient to meet the ordinary demands of the laboratory, the capacity of the apparatus is limited, owing to the fixed area of the nickel cathode of the cell, B. By means of a very simple arrangement, it is possible to greatly increase the capacity of the apparatus with but a slight increase in the expenditure of energy.

In a previous experiment (page 22), it was shown that in spite of the extremely small resistance of the nickel rod, Z, the resistance of the minor circuit between the mercury, M', and the point, z, was still small enough to cause the current of the major circuit to divide, sending a shunt through the minor circuit. It is therefore possible, by placing a variable resistance in the nickel rod, to send, as desired, any proportion of the current of the major circuit through the minor circuit.

The resistance which is required in the rod, to practically shunt the entire current of the major circuit through the minor circuit, is not large. This is due to the low resistance offered by the solution of the pure caustic alkali to the shunted current, and to a gain in the electrical energy at the nickel cathode by the discharge of the cations from the alkali metal in the mercury. This gain in electrical energy is equivalent to the difference in the electro-motor forces which are acquired to electrolyze the solution of the electrolyte in A with two platinum electrodes, and with a platinum anode and a mercury cathode. Electrical energy thus gained greatly aids in balancing the increase in the resistance offered by the pure caustic solution, and the resistance which is placed in the nickel rod. Owing to the low electro-motor force of the cell, B, the addition of comparatively small resistance in the nickel rod practically eliminates the decomposition of the amalgam by the current of the minor circuit.

By this method, the rate of discharge of the amalgam can be regulated to keep pace with the current efficiency of the process, independent of the current employed for the decomposition of the electrolyte in the cell, A. Since the rate of

decomposition of the amalgam by this method is independent of the current density, very high current densities can be profitably employed. Starting with a small per cent of amalgam present in the mercury, by proper regulation, that proportion of the major current can be shunted and made to discharge the amalgam which is equivalent to the current efficiency without either an accumulation or a depletion of the amalgam in the mercury. The process is therefore continuous and requires but little attention.

Comparative tests were made with the apparatus when the above method was used, and when there was no added resistance in the nickel rod. The current was passed through the apparatus from the storage battery whose electro-motor force was kept constant by charging at the same rate as the discharge. Ammeters were placed in the major circuit, in the shunt circuit, and in the circuit of the current through the nickel rod. By means of a rheostat placed in the circuit of the nickel rod, resistance could be varied as desired. With a current of 11 amperes, and no resistance in the nickel rod, the fall in potential was 4.4 volts. Employing the same electro-motor force from the battery as before, and with 95 per cent of the major current shunted through the cell, B, the current fell to 10.2 amperes, while the fall in potential was 4.6 volts.

Evidently this method affords a means of greatly increasing the capacity of a small apparatus without increasing very materially the cost of the pure product.

Conclusions.

The purpose of the investigation is fully realized by the process as described.

A small apparatus required but little attention and afforded an abundant supply for laboratory use.

The purity of the product is sufficient for all laboratory purposes.

Crystals of pure potassium hydroxide can be obtained in quantity as a product in the course of ordinary operation of the apparatus.

Crystals of pure sodium hydroxide can be obtained by cooling the saturated solution produced.

The difficulties and dangers pertaining to the preparation of sodium hydroxide from the metal are avoided, and a product is obtained which is not in any wise inferior to that from the metal.

The high current efficiency obtained and the low electromotive force required in the apparatus greatly diminish the cost of pure sodium and potassium hydroxides.

BIOGRAPHICAL.

Henry Philip Straus was born in Baltimore, Maryland, August 7, 1878. He received his early education in the public schools and City College of Baltimore. In 1898-1902, he entered the Johns Hopkins University, receiving the degree of Bachelor of Arts. In October, 1902, he entered the Johns Hopkins University as a student in chemistry. His subordinate subjects were Physical Chemistry and Mineralogy.

